

**DEHYDROXYLATION OF GLYCEROL TO PROPYLENE GLYCOL OVER
COPPER/ZINC OXIDE-BASED CATALYSTS: EFFECTS OF CATALYST
PREPARATION AND REGENERATION**



Suchart Panyad

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institute Français du Pétrole
2010

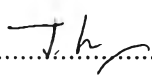
530048

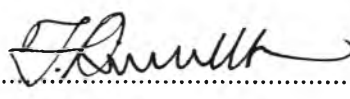
Thesis Title: Dehydroxylation of Glycerol to Propylene Glycol over Copper/Zinc Oxide-based Catalysts: Effects of Catalyst Preparation and Regeneration
By: Suchart Panyad
Program: Petrochemical Technology
Thesis Advisors: Asst. Prof. Siriporn Jongpatiwut
Assoc. Prof. Thirasak Rirksomboon
Asst. Prof. Thammanoon Sreethawong
Prof. Somchai Osuwan

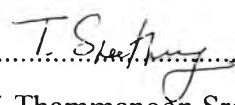
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

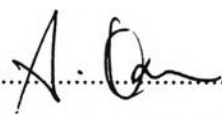

..... Dean
(Asst. Prof. Pomthong Malakul)

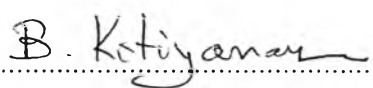
Thesis Committee:

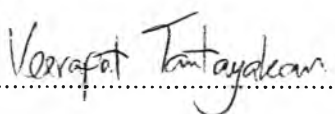

.....
(Asst. Prof. Siriporn Jongpatiwut)


.....
(Assoc. Prof. Thirasak Rirksomboon)


.....
(Asst. Prof. Thammanoon Sreethawong)


.....
(Prof. Somchai Osuwan)


.....
(Asst. Prof. Boonyarach Kitiyanan)


.....
(Dr. Veerapat Tantayakom)

บทคัดย่อ

สุชาติ ปิ่นหยัด : การผลิตโพรพิลีนไกลคอลจากกลีเซอรอลโดยตัวเร่งปฏิกิริยาที่มีทองแดงและสังกะสีออกไซด์เป็นส่วนประกอบพื้นฐาน: ผลกระทบของวิธีเตรียมตัวเร่งปฏิกิริยาและการนำกลับมาใช้ใหม่ (Dehydroxylation of Glycerol to Propylene Glycol over Copper/Zinc Oxide-based Catalysts: Effects of Catalyst Preparation and Regeneration) อาจารย์ที่ปรึกษา: ผศ.ดร. ศิริพร จงผาดูฒิ รศ.ดร. วีรศักดิ์ ฤกษ์สมบูรณ์ ผศ.ดร. ธรรมบุญ ศรีทะวงศ์ ศ.ดร. สมชาย โอสุวรรณ 80 หน้า

กลีเซอรอลเป็นผลิตภัณฑ์พลอยได้หลักจากการผลิตไบโอดีเซลด้วยกระบวนการทรานเอสเตอริฟิเคชัน (Tranesterification) การเพิ่มขึ้นของการผลิตไบโอดีเซลส่งผลให้ปริมาณกลีเซอรอลล้นตลาด ดังนั้นการนำกลีเซอรอลไปเปลี่ยนเป็นสารเคมีที่มีมูลค่าสูงขึ้นเช่น โพรพิลีนไกลคอล โดยผ่านปฏิกิริยาดิไฮดรอกซิเลชันโดยใช้ตัวเร่งปฏิกิริยาก็ถือเป็นทางเลือกหนึ่งที่น่าสนใจ งานวิจัยนี้ได้ศึกษาประสิทธิภาพของตัวเร่งปฏิกิริยาทองแดงและสังกะสีออกไซด์บนอะลูมินา ($\text{Cu-ZnO/Al}_2\text{O}_3$) ในการทำปฏิกิริยาดิไฮดรอกซิเลชัน โดยเตรียมตัวเร่งปฏิกิริยาด้วยเทคนิคที่แตกต่างกัน คือ วิธีเอ็บซุ่ม (IW1) วิธีการตกตะกอนร่วม (COP) และวิธีโซล-เจล (SG) ตัวเร่งปฏิกิริยาที่เตรียมขึ้นทั้งหมดถูกนำไปทดสอบประสิทธิภาพของการทำปฏิกิริยาในเครื่องปฏิกรณ์แบบต่อเนื่องชนิดเบดนิ่งที่อุณหภูมิ 250 องศาเซลเซียส ภายใต้ความดันของไฮโดรเจนที่ 500 ปอนด์ต่อตารางนิ้วเกจ ตัวเร่งปฏิกิริยาเหล่านี้ยังได้ถูกนำไปวิเคราะห์ด้วยเทคนิคต่างๆ เช่น SAA XRF XRD TPR และ TPO จากการศึกษาพบว่า ตัวเร่งปฏิกิริยาที่เตรียมโดยวิธีเอ็บซุ่มมีประสิทธิภาพและความเสถียรที่สูงที่สุดซึ่งอาจเกิดเนื่องมาจากปริมาณการเกิดถ่านโค้กที่ต่ำ รวมถึงโลหะบนพื้นผิวของตัวเร่งปฏิกิริยามีความเสถียรสูง นอกจากนี้ยังพบว่าการเสื่อมสภาพของตัวเร่งปฏิกิริยามีสาเหตุมาจากการทับถมของถ่านโค้กและการรวมตัวกันของโลหะกัมมันต์ ดังนั้น ประสิทธิภาพของตัวเร่งปฏิกิริยาจึงไม่สามารถทำให้ฟื้นคืนด้วยปฏิกิริยาออกซิเดชันของถ่านโค้ก

ABSTRACT

5171023063: Petrochemical Technology

Suchart Panyad: Dehydroxylation of Glycerol to Propylene Glycol over Copper/Zinc Oxide-based Catalysts: Effects of Catalyst Preparation and Regeneration

Thesis Advisors: Asst. Prof. Siriporn Jongpatiwut, Assoc. Prof. Thirasak Rirksomboon, Asst. Prof. Thammanoon Sreethawong, Prof. Somchai Osuwan 80 pp.

Keywords: Dehydroxylation/ Glycerol/1,2-Propanediol/Propylene Glycol/ Cu-ZnO/Al₂O₃/IWI/Co-precipitation/Sol-gel/Regeneration

Glycerol is a major by-product from vegetable oil transesterification to biodiesel. The increase in biodiesel production results in the marketed surplus of glycerol. The catalytic dehydroxylation of glycerol to propylene glycol is one of the most attractive routes to convert glycerol to high value-added products. In this work, the dehydroxylation of glycerol to propylene glycol was investigated over Cu-ZnO/Al₂O₃ catalysts prepared by different techniques—i.e. incipient wetness impregnation (IWI), co-precipitation (COP), and sol-gel (SG) methods. The prepared catalysts were tested for their catalytic activity in a packed-bed reactor at 250 °C and 500 psig under hydrogen atmosphere. Fresh and spent catalysts were characterized by several techniques including SAA, XRF, XRD, TPR, and TPO. Among the catalysts tested, the impregnated Cu-ZnO/Al₂O₃ catalyst provided the highest catalytic performance which could be due to its low coke formation and high stability of metal on surfaces. Furthermore, causes of the catalyst deactivation were found to be the combination of deposited carbon and sintering of active metals. Therefore, the catalytic activity of the Cu-ZnO/Al₂O₃ catalysts cannot be recovered by a simple method for coke removal.

ACKNOWLEDGEMENTS

This work would not have been possible without the assistance of the following individuals.

First of all, I greatly appreciate Asst. Prof. Siriporn Jongpatiwut, Assoc. Prof. Thirasak Rirksomboon, Asst. Prof. Thammanoon Sreethawong, Prof. Somchai Osuwan, my thesis advisors, for providing invaluable recommendations, creative comments, and kindly support throughout the course of this research work.

I would like to thank Asst. Prof. Boonyarach Kitiyanan and Dr. Veerapat Tantayakom for their kind advice and for being my thesis committee.

I am grateful for the partial scholarship and partial funding of the thesis work provided by the Petroleum and Petrochemical College, and by the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

Special appreciation goes to all of the Petroleum and Petrochemical College's staff who gave help in various aspects, especially the Research Affairs staff who kindly help with the analytical instruments used in this work.

For my friends at PPC, I would like to give special thanks for their friendly support, encouragement, cheerfulness, and assistance. Without them, two years in the College would have been meaningless for me. I had the most enjoyable time working with all of them.

Finally, I am deeply indebted to my parents and my family for their unconditionally support, love, and understanding.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	x
CHAPTER	
I INTRODUCTION	1
II LITERATURE REVIEW	3
2.1 Glycerol	3
2.2 Industrial Production of Glycerol	4
2.3 Glycerol Conversion into Valuable Chemicals	5
2.4 Selective Hydrogenolysis of Glycerol to Propanediols	6
2.5 Production of 1,2-Propanediol from Glycerol	8
2.5.1 Biocatalyst	9
2.5.2 Homogeneous Catalyst	10
2.5.3 Heterogeneous Catalyst	11
2.6 Preparation of Supported Metal Catalysts	17
2.6.1 Impregnation	18
2.6.2 Precipitation	18
2.6.3 Sol–Gel Method	19
2.7 Deactivation and Regeneration	22
2.7.1 Poisoning	24
2.7.2 Fouling	26
2.7.3 Thermal Degradation	27
2.7.4 Mechanical Deactivation	29

CHAPTER	PAGE
2.7.5 Corrosion/leaching	30
2.8 Criteria to Ensure Ideal Behaviors in Trickle-bed Reactors	32
III EXPERIMENTAL	36
3.1 Materials	36
3.1.1 Chemicals	36
3.1.2 Gas	37
3.2 Equipment	37
3.3 Methodology	37
3.3.1 Catalyst Preparation	37
3.3.2 Catalyst Characterization	38
3.3.3 Catalytic Activity Measurement	41
3.3.4 Catalyst Regeneration	43
IV RESULTS AND DISCUSSION	44
4.1 Incipient Wetness Impregnation (IWI) and Co-precipitation (COP)	44
4.2 Sol-Gel Method	46
4.2.1 Effect of Aluminium isopropoxide (AIP) to Water Molar Ratio	46
4.2.2 Effect of Calcination Temperature	47
4.2.3 Effect of Solution pH	52
4.3 Effects of Catalyst Preparation Technique on Catalytic Performance	53
4.4 Catalyst Regeneration	56
V CONCLUSIONS AND RECOMMENDATIONS	64
5.1 Conclusions	64
5.2 Recommendations	64

CHAPTER	PAGE
REFERENCES	65
APPENDIX	70
Appendix A Analysis Report Obtained from X-ray Fluorescence Spectrometer	70
Appendix B Copper Leaching Calculation from AAS Analysis	71
Appendix C Flow Criteria Calculation	75
CURRICULUM VITAE	80

LIST OF TABLES

TABLE	PAGE	
2.1	Summary of conversion of glycerol, yield and selectivity of propylene glycol from glycerol over various metal catalysts	12
2.2	Mechanisms of catalyst deactivation	23
2.3	Common poisons classified according to chemical structure	25
2.4	Effects of important reaction and catalyst variables on sintering rates of supported metals based on GPLE data	29
4.1	Catalyst weights and volumes obtained by different preparation methods	44
4.2	BET surface areas of the Cu-ZnO/Al ₂ O ₃ catalysts calcined at different temperatures	51
4.3	Bulk density of the catalysts prepared by different methods	53
4.4	Percentages of carbon deposition and physical properties of the fresh (calcined) and spent Cu-ZnO/Al ₂ O ₃ catalysts after de-coking	61
4.5	The compositions of the fresh (calcined) and spent Cu-ZnO/Al ₂ O ₃ catalysts prepared by different methods	62
4.6	Percentage of copper leaching after 4 hours of reaction determined by XRF and AAS	62
A1	The concentration of element in the fresh and spent Cu-ZnO/Al ₂ O ₃ catalysts prepared by different methods	70
C1	Summary of flow criteria used in this study	76

LIST OF FIGURES

FIGURE		PAGE
2.1	Chemical structure and some properties of glycerol.	3
2.2	Overall reaction for production of biodiesel through vegetable oil methanolysis.	4
2.3	Processes of catalytic conversion of glycerol into useful chemicals.	5
2.4	Different routes to 1,3-propanediol starting from ethene, propene or glycerol.	8
2.5	Comparison of the reaction routes to 1,2-propanediol starting from propene or glycerol.	9
2.6	Reaction mechanism for conversion of glycerol to propylene glycol proposed by Montassier <i>et al.</i>	10
2.7	Possible reaction routes for catalytic hydrogenolysis of glycerol proposed by Chaminand <i>et al.</i>	11
2.8	Proposed reaction mechanism for conversion of glycerol to propylene glycol.	13
2.9	Reaction scheme of glycerol hydrogenolysis and degradation reactions.	14
2.10	Proposed bifunctional glycerol hydrogenolysis reaction pathways.	15
2.11	Reaction route for the hydrogenolysis of glycerol to glycols.	16
2.12	Schematic diagram showing the various steps of a sol-gel process.	20
2.13	Time scale of deactivation of various catalytic processes.	22
2.14	Major types of deactivation in heterogeneous catalysis.	24
2.15	Conceptual model of poisoning by sulfur atoms of a metal surface during ethylene hydrogenation.	24

FIGURE		PAGE
2.16	Three kinds of poisoning behavior in terms of normalized activity vs. normalized poison concentration.	26
2.17	Two conceptual models for crystallite growth due to sintering by (A) atomic migration or (B) crystallite migration.	28
2.18	Relation between the Peclet particle and Reynolds particle numbers for single-phase and trickle flow.	33
3.1	Flow diagram of the system used for dehydroxylation of glycerol.	42
4.1	Glycerol conversion as a function of time on stream over Cu-ZnO/Al ₂ O ₃ catalysts prepared by different preparation methods (LHSV).	45
4.2	Glycerol conversion as a function of time on stream over Cu-ZnO/Al ₂ O ₃ catalysts prepared by different preparation methods (WHSV).	45
4.3	(a) Glycerol conversion and (b) selectivity to propylene glycol as a function of time on stream over Cu-ZnO/Al ₂ O ₃ catalysts prepared by different AIP to water molar ratios.	47
4.4	(a) Glycerol conversion and (b) selectivity to propylene glycol as a function of time on stream for the Cu-ZnO/Al ₂ O ₃ catalysts prepared by sol-gel method and calcined at different temperatures.	48
4.5	TPR profiles of the Cu-ZnO/Al ₂ O ₃ catalysts prepared by sol-gel method and calcined at different temperatures.	49
4.6	XRD patterns of the (a) fresh and (b) reduced Cu-ZnO/Al ₂ O ₃ catalysts prepared by sol-gel method and calcined at different temperatures.	50
4.7	Glycerol conversion as a function of time on stream over Cu-ZnO/Al ₂ O ₃ catalysts prepared by different solution pH.	52

FIGURE		PAGE
4.8	Plot of (a) glycerol conversion and (b) propylene glycol selectivity as a function of time on stream over Cu-ZnO/Al ₂ O ₃ catalysts prepared by different preparation methods.	54
4.9	Temperature-programmed oxidation (TPO) profiles of the spent Cu-ZnO/Al ₂ O ₃ catalysts prepared by different preparation methods.	55
4.10	Time course of conversion of glycerol over the (a) fresh, and (b) regenerated Cu-ZnO/Al ₂ O ₃ catalysts.	56
4.11	TPR profiles of the fresh and spent Cu-ZnO/Al ₂ O ₃ catalysts prepared by different methods.	57
4.12	XRD patterns of the reduced Cu-ZnO/Al ₂ O ₃ catalysts prepared by different methods.	58
4.13	TPR profiles of the impregnated Cu-ZnO/Al ₂ O ₃ catalysts at different conditions and the CuO reference standard.	59
4.14	XRD patterns of the impregnated Cu-ZnO/Al ₂ O ₃ catalysts at different conditions.	60
C1	(a) Glycerol conversion and (b) selectivity to propylene glycol as a function of time on stream for the co-precipitated Cu-ZnO/Al ₂ O ₃ at different dilution ratios.	75